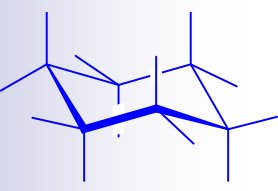
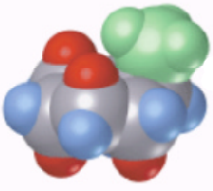


Aliphatic Hydrocarbons

Jully Tan
School of Engineering


Learning Outcome

At the end of the lecture, students will be able to:

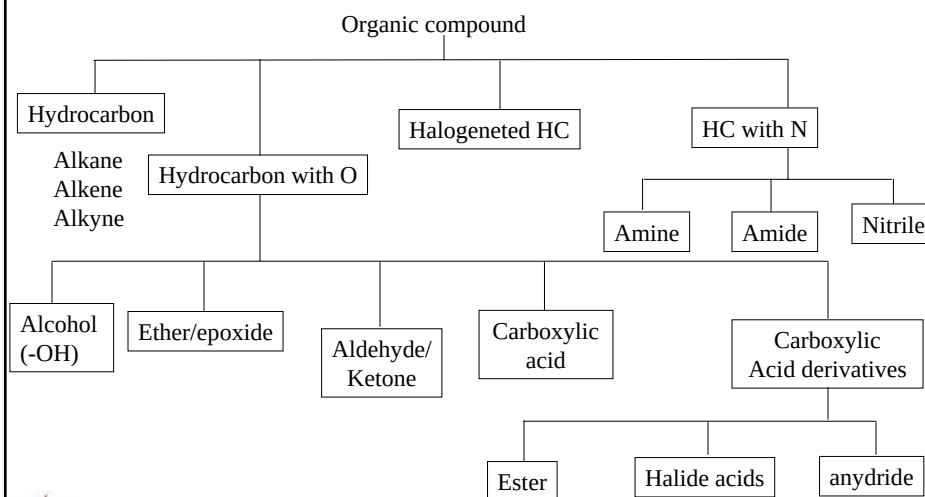
- Understand the family under organic compounds.
- Explain the aliphatic hydrocarbon or alkanes specifically by its structure, physical and chemical properties.
- Naming the organic compound especially for alkanes according to IUPAC method.
- Explain the type of isomer in organic compound and draw the different isomer structures of the compound.
- Explain the different type of the synthesis of alkanes and reaction of alkanes specifically:
 - ☐ Halogenation
 - ☐ Combustion
 - ☐ Hydrogenation of alkenes
 - ☐ Reaction of Alkyl Halides with organometals
 - ☐ Reduction of Alkyl Halides



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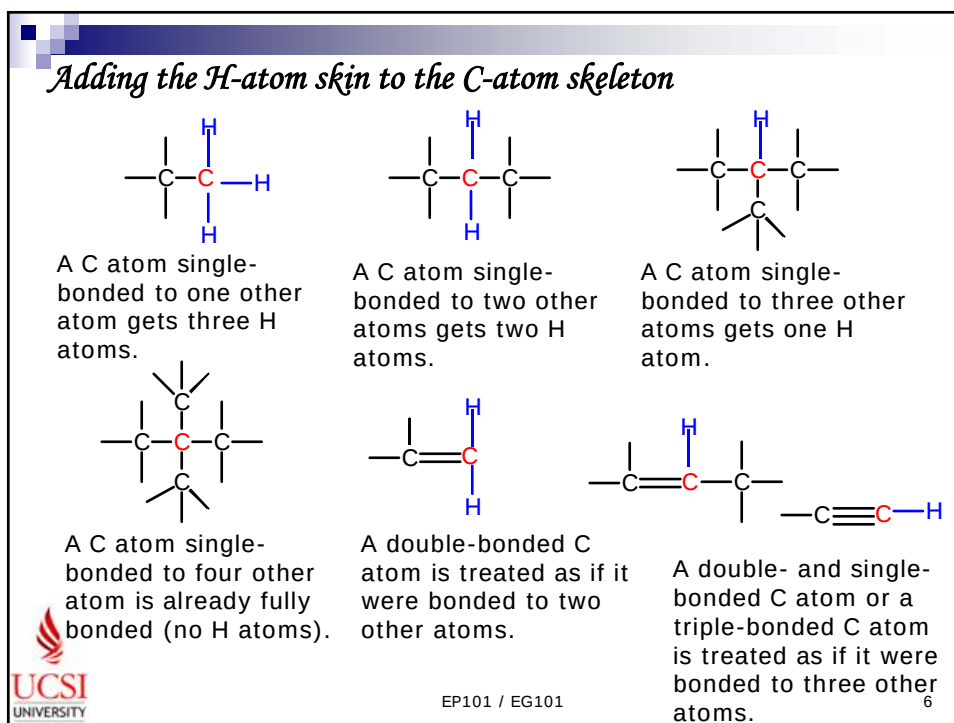
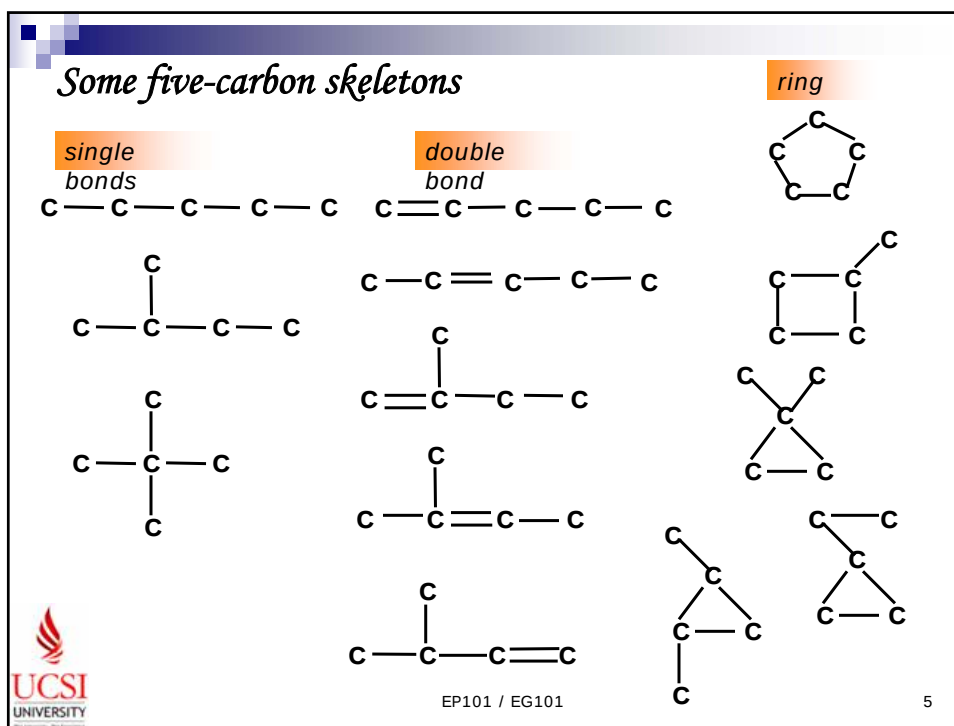
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Classes of Organic Compounds



Overview

- Hydrocarbon
 - Composed entirely of C and H atoms.
 - Has 3 main categories
 - Aliphatic - straight chain HC
 - Cyclic - ring shape HC
 - Aromatic – HC derived from benzene ring.
- Each C can form a maximum of four single bonds, **OR** two single and one double bond, **OR** one single and triple bond.

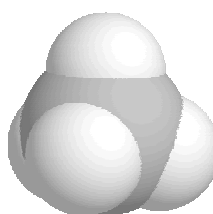
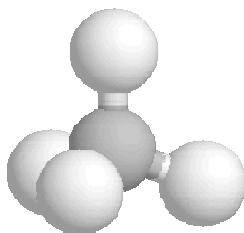
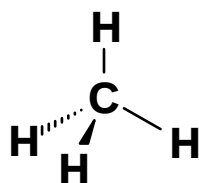


Functional Group	Compound Type	Suffix or Prefix of Name	Example		Systematic Name (Common Name)
	alkene	-ene			ethene (ethylene)
	alkyne	-yne			ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
	haloalkane	halo-			chloromethane (methyl chloride)
	amine	-amine			ethylamine
	aldehyde	-al			ethanal (acetaldehyde)

Functional Group	Compound Type	Suffix or Prefix of Name	Example		Systematic Name (Common Name)
	ketone	-one			2-propanone (acetone)
	carboxylic acid	-oic acid			ethanoic acid (acetic acid)
	ester	-oate			methyl ethanoate (methyl acetate)
	amide	-amide			ethanamide (acetamide)
	nitrile	-nitrile			ethanenitrile (acetonitrile, methyl cyanide)

Alkanes, C_nH_{2n+2}

- carbon-carbon single bond: s (head-on) overlap of carbon sp^3 orbitals
- saturated hydrocarbons; only C-C and C-H bonds
- Alkane: a saturated hydrocarbon whose carbons are arranged in a chain. Saturated hydrocarbon: a hydrocarbon containing only single bonds.
- Aliphatic hydrocarbon: another name for an alkane: aliphatic, "fat"

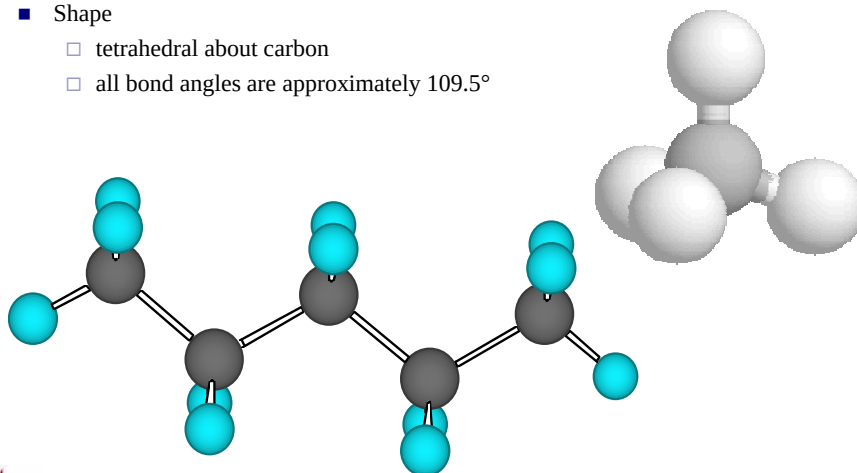


1. Molecular Formula of Alkanes

Name	No of C	Molecular Formula
Methane	1	
Ethane	2	
Propane	3	
Butane	4	
Pentane	5	
Hexane	6	
Heptane	7	
Octane	8	
Nonane	9	
Decane	10	

Structure

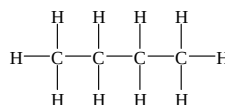
- Shape
 - ☐ tetrahedral about carbon
 - ☐ all bond angles are approximately 109.5°



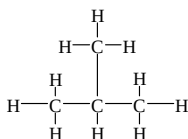
Branching vs. No Branching

- Isomer: same chemical formula, but different structure.
- There are 2 isomeric butanes

- ☐ n-butane
- ☐ C_4H_{10}
- ☐ n means “normal” or in a straight chain



- ☐ isobutane
- ☐ C_4H_{10}

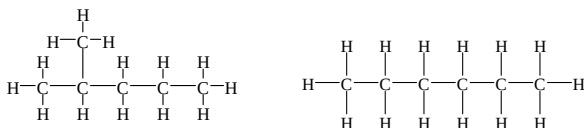


Find the Isomers of C_6H_{14}

Draw the structures for C_6H_{14} starting with the longest chain (6 in a row)

...next draw all structures with 5 carbons in the longest chain (substitute for the H s)

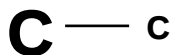
...then substitute for other H s



Classification of C & H

- Primary (1°) C: a carbon bonded to one other carbon
 - 1° H: a hydrogen bonded to a 1° carbon
- Secondary (2°): a carbon bonded to two other carbons
 - 2° H: a hydrogen bonded to a 2° carbon
- Tertiary (3°) C: a carbon bonded to three other carbons
 - 3° H: a hydrogen bonded to a 3° carbon
- Quaternary (4°) C: a carbon bonded to four other carbons

Degree of Substitution



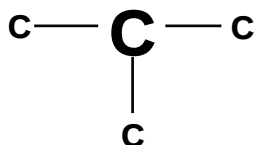
PRIMARY

CONNECTED TO ONE
OTHER CARBON



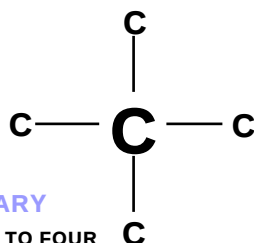
SECONDARY

CONNECTED TO TWO
OTHER CARBONS



TERTIARY

CONNECTED TO THREE
OTHER CARBONS



QUATERNARY

CONNECTED TO FOUR
OTHER CARBONS

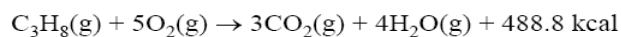
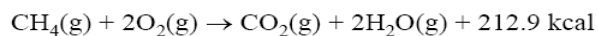


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2. Chemical Properties

- Not reactive compound:
 - Alkanes are the least reactive among all other organic comp. They do not usually react with strong acids or bases, or with most oxidizing or reducing agents.
- Highly combustible compound
 - Alkanes can burn easily in combustion reactions and releasing high energy.



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3. Physical Properties, Density & Solubility

- Alkanes physical forms as gas, liquid and solid.
 - C_1 - C_4 -Gas
 - C_5 - C_{17} -Liquid
 - C_{18} and above -Solid
- Only dissolves in organic solvent, such as benzene, CCl_4 , but do not dissolve in water (hydrophobic).
- Alkane is less density than water. (near 0.7 g/mL)

Why do alkane do not dissolve in water?

4. Boiling Point

- Both bp and mp increase with increasing carbon number for straight-chain alkanes with formula C_nH_{2n+2}
- Branching tends to **raise the melting point** and **lower the boiling point**. Why??

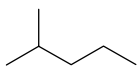
Hint: surface area of alkane.



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- Branching tends to **lower the boiling point** and **raise the melting point**



BP 60°C

MP -154°C



58°C

-135°C



50°C

-98°C

Explanation:

MP Branching reduces the flexibility of the molecule which reduces the entropy term ΔS in the equation $T_{mp} = \Delta H / \Delta S$. Since ΔS is in the denominator, T_{mp} increases. The structure of the alkane packed better into a compact 3D structure which is said the atom are bonded more tightly and need higher T to transform the alkane from solid to liquid phase.

BP Branching reduces surface area (more compact structure), and therefore Van der Waals dispersion forces which control boiling point for these molecules been reduces. Less energy to overcome these reactions to transform liquid to gas phase.

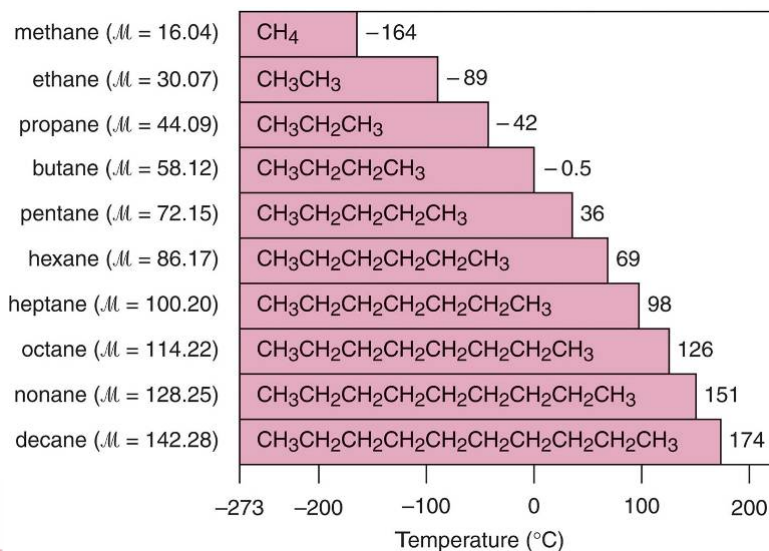
Answer: Solubility – alkanes are nonpolar molecules and therefore **insoluble in water**, which is polar. Alkanes are **hydrophobic**.



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Boiling points of the first 10 unbranched alkanes



Boiling Points of Alkanes

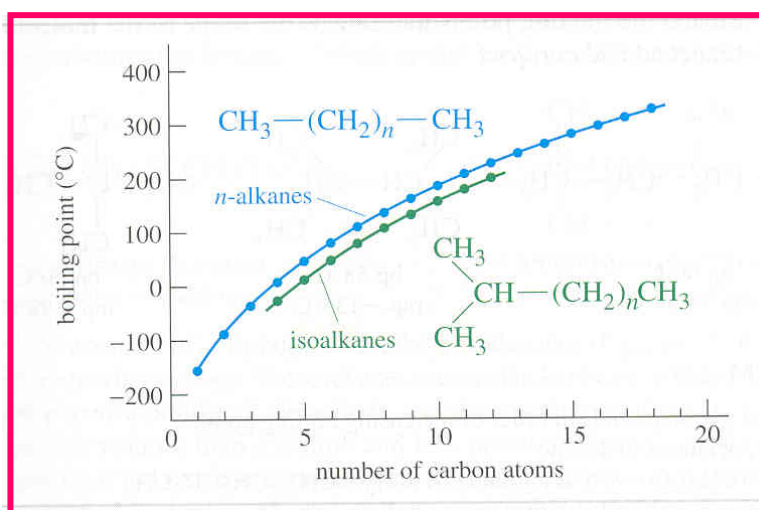
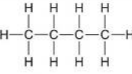
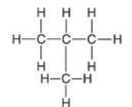
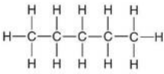
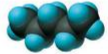
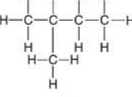
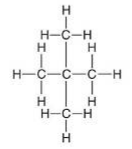


Table 15.3 The Constitutional Isomers of C_4H_{10} and C_5H_{12}

Systematic Name (Common Name)	Condensed Formula	Expanded Formula	Space-filling Model	Density (g/mL)	Boiling Point ($^{\circ}\text{C}$)
Butane (<i>n</i> -butane)	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$ 			0.579	−0.5
2-Methylpropane (isobutane)	$\text{CH}_3\text{—CH—CH}_3$ CH_3 			0.549	−11.6
Pentane (<i>n</i> -pentane)	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ 			0.626	36.1
2-Methylbutane (isopentane)	$\text{CH}_3\text{—CH—CH}_2\text{—CH}_3$ CH_3 			0.620	27.8
2,2-Dimethylpropane (neopentane)	CH_3 $\text{CH}_3\text{—C—CH}_3$ CH_3 			0.614	9.5



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Sources

- 2 main sources are petroleum & natural gas

TABLE Major Fractions Obtained from Distillation of Crude Petroleum

Boiling Range ($^{\circ}\text{C}$)	Number of Carbons	Fraction	Use
under 30°	2–4	petroleum gas	LP gas for heating
30° – 180°	4–9	gasoline	motor fuel
160° – 230°	8–16	kerosene	heat, jet fuel
200° – 320°	10–18	diesel	motor fuel
300° – 450°	16–30	heavy oil	heating, lubrication
$>300^{\circ}$ (vacuum)	>25	petroleum “jelly,” paraffin “wax”	
residue	>35	asphalt	



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Nomenclature



International Union of Pure and Applied Chemistry

colloquially:
"eye-you-pac"



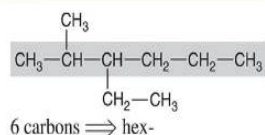
International Union of Pure and Applied Chemistry (IUPAC)

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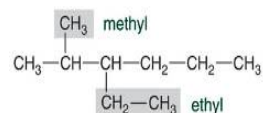
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Table 15.2 Rules for Naming an Organic Compound

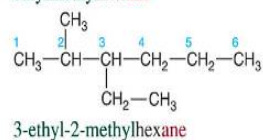
- Naming the longest chain (root)
 - Find the longest *continuous* chain of C atoms.
 - Select the root that corresponds to the number of C atoms in this chain.
- Naming the compound type (suffix)
 - For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
 - If the chain forms a ring, the name is preceded by *cyclo-*.
- Naming the branches (prefix)
 - Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
 - Branch names precede the chain name. When two or more branches are present, name them in *alphabetical* order.
 - To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the chain C to which that branch is attached.
 - If the compound has no branches, the name consists of the root and suffix.



hex- + *-ane* $\Rightarrow$ hexane



ethylmethylhexane



1. Numerical Roots for Carbon Chains and Branches

PREFIX + **ROOT (Parent)** + SUFFIX

Roots / Parent	Number of C atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Roots / Parent	Number of C atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

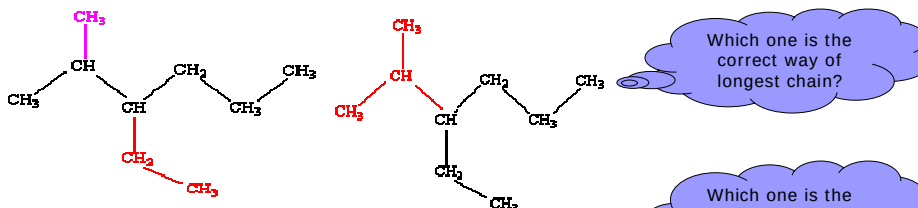


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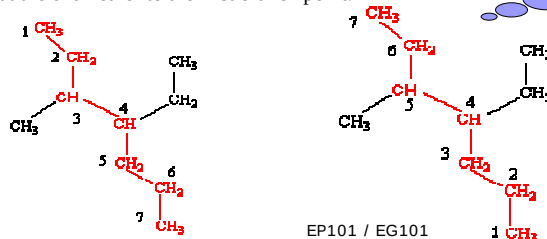
STEP 1 : Find the parent hydrocarbon

- Find longest continuous chain of carbons and use as parent name.
- If 2 chains have same number of carbons, choose the one with the more branch points.



STEP 2 : Number the atoms in parent chain

- Begin at the end nearer to the first branch point.

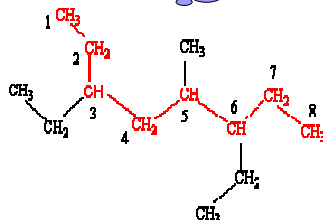
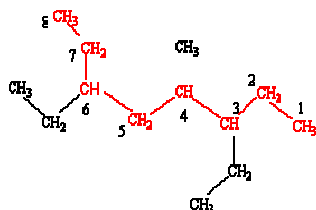


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2. If branching occurs at equal distance from both ends, begin numbering at the end nearer the second branch point.

Which one is the correct way of numbering the atom of the chain?



2. Naming the Compound Types of Suffix

PREFIX + ROOT (Parent) + SUFFIX

- Suffix is the type of the family of that specifies organic compound.
- For example, alkanes, alkene and etc.

3. Identify Prefix of the Chain

Alkyl group, R-	Common name	Complex name (if different)
CH_3 -	methyl-	
CH_3CH_2 -	ethyl-	
$\text{CH}_3\text{CH}_2\text{CH}_2$ -	propyl-	
$(\text{CH}_3)_2\text{CH}$ -	isopropyl-	(1-methylethyl)-
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ -	butyl-	
$\text{CH}_3\text{CH}_2\text{CHCH}_3$	sec-butyl- or s-butyl	(1-methylpropyl)-
$(\text{CH}_3)_2\text{CHCH}_2$ -	isobutyl	(2-methylpropyl)-
$(\text{CH}_3)_3\text{C}$ -	tert-butyl or t-butyl	(1,1-dimethylethyl)-

pentyl $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

isopentyl $-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

neopentyl $-\text{CH}_2\text{C}(\text{CH}_3)_3$

Structural formula	Name
CH_3 -	methyl-
CH_3CH_2 -	ethyl-
$\text{CH}_3\text{CH}_2\text{CH}_2$ -	propyl- or n-propyl
$(\text{CH}_3)_2\text{CH}$ -	isopropyl-
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ -	butyl- or n-butyl
$\text{CH}_3\text{CHCH}_2\text{CH}_3$	sec-butyl- or s-butyl
$(\text{CH}_3)_2\text{CHCH}_2$ -	isobutyl
$(\text{CH}_3)_3\text{C}$ -	tert-butyl or t-butyl

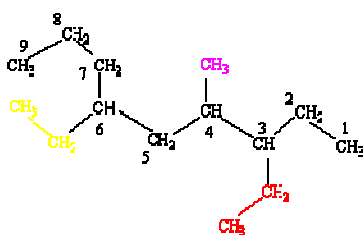


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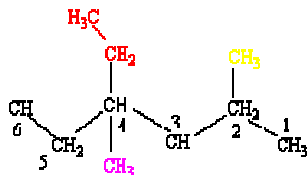
STEP 1 : Identify and number the substituents

1. Give each substituent a number that corresponds to its position on the parent chain.



Substituents		
C3	CH_2CH_3	3-ethyl
C4	CH_3	4-methyl
C6	CH_2CH_3	6-ethyl

2. Two substituents on the same carbon gets the same number



Substituents :		
C2	CH_3	2-methyl
C4	CH_3	4-methyl
C4	CH_2CH_3	4-ethyl



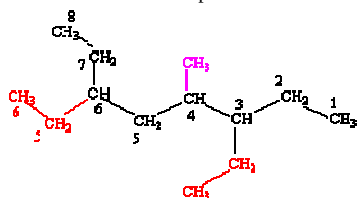
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STEP 2: Write the name as a single word (follow alphabetical order)

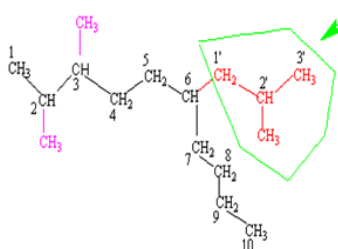
1. Use hyphens to separate prefixes and commas to separate numbers or more identical substituents are present, use multipliers (di, tri, tetra)

- Note : the multipliers are not use for alphabetizing.



Name a complex substituent as if it were a compound and put them in parentheses

Begin numbering of the complex substituent from the point of attachment to the parent chain.



Parent : decane

Substituents :

C2 2-methyl

C3 3-methyl

C6 2-methylpropyl

2,3-dimethyl-6-(2-methylpropyl)decane

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Naming & Drawing Cyclic Alkanes

Name of branching group or substitute (if any)

+ Use Prefix “cyclo”

+

Parent name

Parent Name = longest continuous chain of carbon atoms

Cyclo = parent chain forms a ring

STEP 1: Find parent

- If number of carbon atoms in the ring is larger than the number in the largest substituent, the compound is an alkyl-substituted cycloalkane.
- If the number of carbon atoms in the ring is smaller than the number in the largest substituent, the compound is a cycloalkyl-substituted alkane.

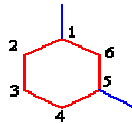
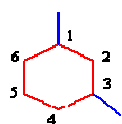


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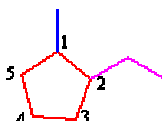
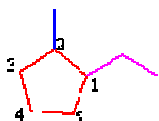
■ **STEP 2: Number the substituents and write the name**

1. Start at a point of attachment and number the substituents so that the second substituent has the lowest possible number.
2. If necessary, proceed to the next substituent until a point of difference is found.

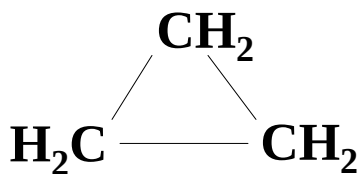


Which one is the correct way of numbering the atom of the chain?

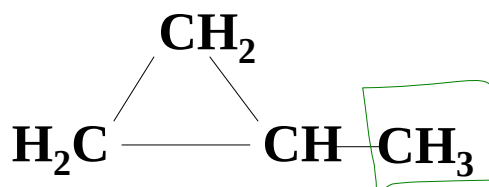
3. If 2 or more substituents might potentially receive the same number, number them alphabetical priority. Treat halogens as if they are alkyl groups.



Which one is the correct way of numbering the atom of the chain?



1. What is the parent name?
Propane (Longest chain is 3 carbons)
2. Is the parent chain in a ring?
Yes
Correct name is: cyclopropane



Parent name is **cyclopropane**.

What is the branching group? **Methyl -CH₃**

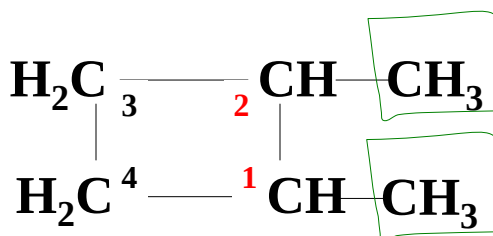
Correct name is: **methylcyclopropane**

Note: The number (1) is not needed to identify the place of the substituent if only one is present in the molecule.



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Parent name is **cyclobutane**.

What is the branching group? **Methyl -CH₃**

Correct name is: **1, 2-dimethylcyclobutane**

Note: The first named substituent is arbitrarily given the number one (1) position



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Reaction of Alkanes & Synthesis of Alkanes

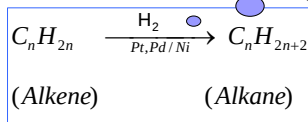
Synthesis	Reaction
■ Hydrogenation of Alkenes	■ Halogenation
■ Reduction of Alkyl Halides	■ Combustion
■ Reaction of Alkyl Halides with organometals	■ Cracking & hydrocracking



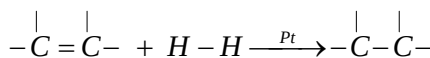
Synthesis of Alkanes:

1. Hydrogenation of Alkenes

- Catalytic hydrogenation of alkene to form alkanes.
- General rxn eqn:



What is the function of the catalyst??



- It takes place under heterogeneous (more than 1 phase) system; the alkene & H₂ are adsorbed on the metallic surface. Therefore they are weakened (both multiple bond and H-H bond).
- The H₂ will add to the same side of the multiple bond: cis-condition.

Synthesis of Alkanes:

2. Reduction of Alkyl Halides

A: Hydrolysis by Grignard Reagent

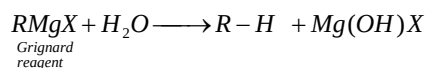
- Grignard reagent: prepared by treating an alkyl/aryl halide with magnesium metal in dry ether. General eqn. of the preparing of Grignard reagent



R: alkyl / aryl group

- Grignard reagent is a reactive reagent. It can react with H₂O to form Alkane.

X: Cl, Br, I



B: Reduction by metal & acid

- General eqn.
$$RX \xrightarrow[\text{CH}_3\text{COOH}]{\text{Zn}} RH$$
- Eg. Reduction of Chloro-cyclohexane with Zn & acetic acid able to produce 83% of cyclohexane.
- Alkyl halide as well react with Lithium aluminium hydride (LiAlH_4)

$$RX \xrightarrow{\text{LiAlH}_4} RH$$

- Tetrahydroaluminate ion will react with alkyl halide to produce alkane

$$\begin{array}{c} \text{H} - \text{Al}^- - \text{H} \\ | \\ \text{tetrahydroaluminate} \end{array} + \begin{array}{c} \text{H} - \text{C} - \text{X} \\ | \\ \text{Alkyl Halide} \end{array} \longrightarrow \begin{array}{c} \text{H} - \text{Al} \\ | \\ \text{Alkane} \end{array} + \begin{array}{c} \text{H} - \text{C} - \text{H} \\ | \\ \text{Alkane} \end{array} + \text{X}^-$$

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3. Reaction of Alkyl Halides with organometals

- Alkane can be synthesis via nucleophilic substitution reaction between alkyl halide and a negative nucleophile.
- The carbon in the polar carbon-halogen bond is positive, therefore the negative nucleophile is attracted to it.

$$R_2CuLi + R'X \longrightarrow R-R' + RCu + LiX$$

Litium dialkyl Cuprum

$$RX \xrightarrow{Li} + R-Li \xrightarrow{CuX} R_2CuLi + \xrightarrow{R'X} + R-R$$



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Reaction of Alkane

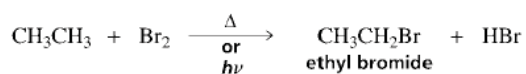
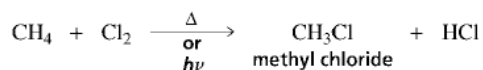
1. Halogenation

◆ Chlorination and Bromination

Formation of alkyl chlorides and alkyl bromides

Reaction takes place at high energies

High temps Δ
Intense light $h\nu$



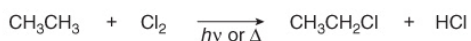
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Halogenation of Alkanes

- Radical halogenation has three distinct parts.

Overall
reaction



- ◆ **Initiation:** Two radicals are formed by homolysis of a σ bond and this begins the reaction.
- ◆ **Propagation:** A radical reacts with another reactant to form a new σ bond and another radical.
- ◆ **Termination:** Two radicals combine to form a stable bond. Removing radicals from the reaction mixture without generating any new radicals stops the reaction.

- A mechanism such as radical halogenation that involves two or more repeating steps is called a **chain mechanism**.
- The most important steps of radical halogenation are those that lead to product formation—the **propagation steps**.

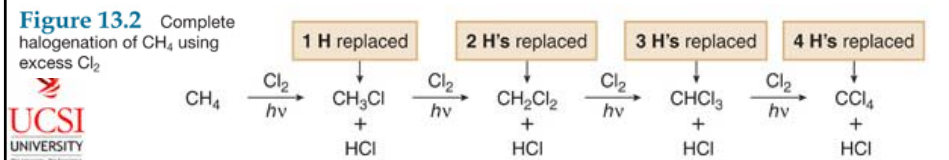


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Halogenation of Alkanes

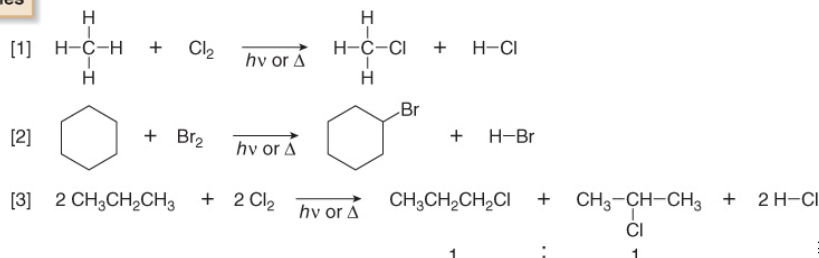
- When a single hydrogen atom on a carbon has been replaced by a halogen atom, **monohalogenation** has taken place.
- When excess halogen is used, it is possible to replace more than one hydrogen atom on a single carbon with halogen atoms.
- Monohalogenation can be achieved experimentally by adding halogen X_2 to an excess of alkane.
- When asked to draw the products of halogenation of an alkane, draw the products of monohalogenation only, unless specifically directed to do otherwise.



Halogenation of Alkanes

- In the presence of heat or light, alkanes react with halogens to form alkyl halides.
- Halogenation of alkanes is a radical substitution reaction.
- Halogenation of alkanes is only useful with Cl_2 or Br_2 . Reaction with F_2 is too violent, and reaction with I_2 is too slow to be useful.
- With an alkane that has more than one type of hydrogen atom, a mixture of alkyl halides may result.

Examples



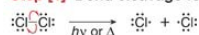


MECHANISM 13.1

Radical Halogenation of Alkanes

Initiation

Step [1] Bond cleavage forms two radicals.

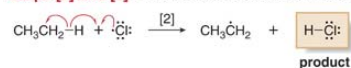


◆ The reaction begins with homolysis of the weakest bond in the starting materials using energy from light or heat.

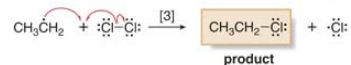
◆ Thus, the Cl–Cl bond ($\Delta H^\circ = 58 \text{ kcal/mol}$), which is weaker than either the C–C or C–H bond in ethane ($\Delta H^\circ = 88$ and 98 kcal/mol , respectively), is broken to form two chlorine radicals.

Propagation

Steps [2] and [3] One radical reacts and a new radical is formed.



◆ The Cl· radicals are highly reactive (they lack an octet of electrons), so they abstract a hydrogen atom from ethane (Step [2]). This forms H–Cl and leaves one unpaired electron on carbon, generating the ethyl radical ($\text{CH}_3\text{CH}_2\cdot$).



◆ $\text{CH}_3\text{CH}_2\cdot$ is highly reactive, so it can abstract a chlorine atom from Cl_2 (Step [3]), forming $\text{CH}_3\text{CH}_2\text{Cl}$ and a new chlorine radical ($\text{Cl}\cdot$).

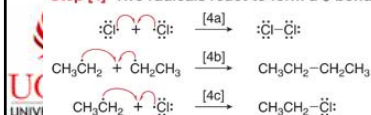
Repeat Steps [2], [3], [2], [3], again and again.

◆ The Cl· radical formed in Step [3] is a reactant in Step [2], so Steps [2] and [3] can occur repeatedly without an additional initiation reaction (Step [1]).

◆ In each propagation step, one radical is consumed and one radical is formed. The two products— $\text{CH}_3\text{CH}_2\text{Cl}$ and HCl—are formed during propagation.

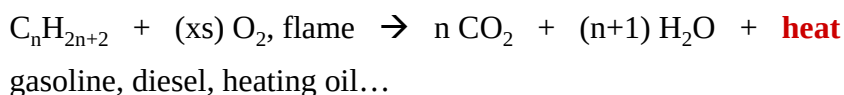
Termination

Step [4] Two radicals react to form a σ bond.



◆ To terminate the chain, two radicals react with each other in one of three ways (Steps [4a, b, and c]). Because these reactions remove reactive radicals and form stable bonds, they prevent further propagation via Steps [2] and [3].

2. Combustion



3. Pyrolysis (cracking)



Used to increase the yield of gasoline from petroleum. Higher boiling fractions are “cracked” into lower boiling fractions that are added to the raw gasoline. The alkenes can be separated and used in to make plastics.



REVISION CHECK

What should you be able to do?

Recall and explain the physical properties of alkanes

Recall and explain the types of isomerism found in alkanes

Recall and explain why alkanes undergo chlorination free radical reaction

Write balanced equations representing the reactions taking place in this section

CAN YOU DO ALL OF THESE?

NO

YES

